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On the mobility of potassium ions in SiO_2

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A new method to measure the mobility of K^+ ions in SiO_2 is proposed. The method is based on the TVS (triangular voltage sweep) technique at temperatures above 300°C. The dependence of the voltage at which the current maximum occurs on the sweep rate provides the mobility at a particular temperature. Measurements at different temperatures show that the mobility of K^+ ions in SiO_2 can be described by $\mu(T) = (17.46/T)\exp(-1.09/kT)$ $cm^2V^{-1}s^{-1}$ in the temperature region 300–450°C.

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I. INTRODUCTION

The role of alkali ions in SiO_2 is very important for the stability and reliability of silicon devices. When these ions move in the silicon dioxide layer they cause the operating characteristics of semiconductor devices to drift from their initial values.

In the study of the physical aspects of this process, it is necessary to know the mobility of the mobile ions. Recently, the mobility of K^+ ions in dry-grown oxide layers was measured by Stagg.[1] This was carried out by measuring the transit time of the ions at a certain temperature after changing the polarity of the field across the oxide.

In this paper we present a more simple method to measure the mobility of K^+ ions. The method is based on the shift of the current maximum in a TVS curve as a function of the sweep rate. This enables us to measure the mobility of K^+ ions at high temperatures (300–450 °C). Our extrapolated results and those found by Stagg agree very well.

II. THE MODEL

An MOS structure is subjected to a gate voltage V_G and brought to an elevated temperature. The movement of mobile ions through silicon dioxide is modeled as follows. The oxide is assumed to be homogeneous and to contain trapping sites only at the interfaces. Once an ion is thermally emitted from a trap, it drifts under influence of the field to the other side of the oxide. For simplicity we will not consider effects caused by field-assisted emission, diffusion, and the interactions of the ions.

It has been shown that two types of ions, Na^+ and K^+, are mainly responsible for the measured ionic movement in the temperature region 30–400 °C and for fields < 1 MV/cm.[2,3] Two measuring methods reflect primarily the emission and the drift part of the model: the thermally stimulated ionic current (TSIC) technique and the triangular voltage sweep (TVS) method, respectively.[4] This last method was used mainly to test quasistatic models but it is well suited for determining the concentration of the different mobile ionic species at higher sweep rates.

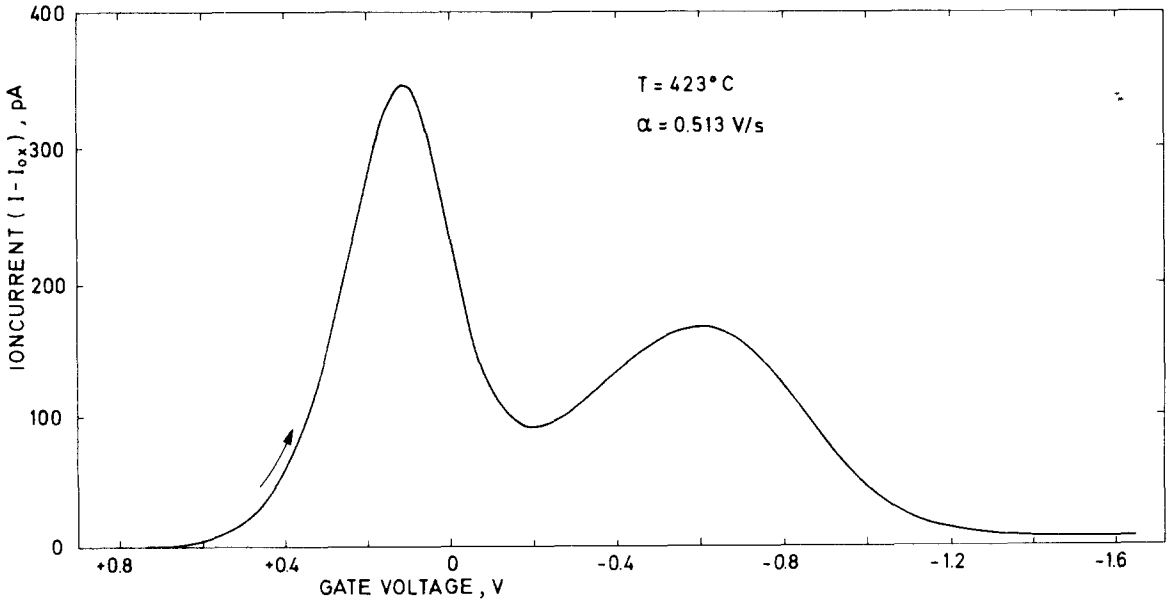

FIG. 1. Example of a typical nonquasistatic TVS measurement. The ions move from the silicon towards the aluminum interface. The current due to the oxide capacitance (I_{ox}) is suppressed. The left peak is due to mobile Na^+ ions; the right one due to K^+ ions.

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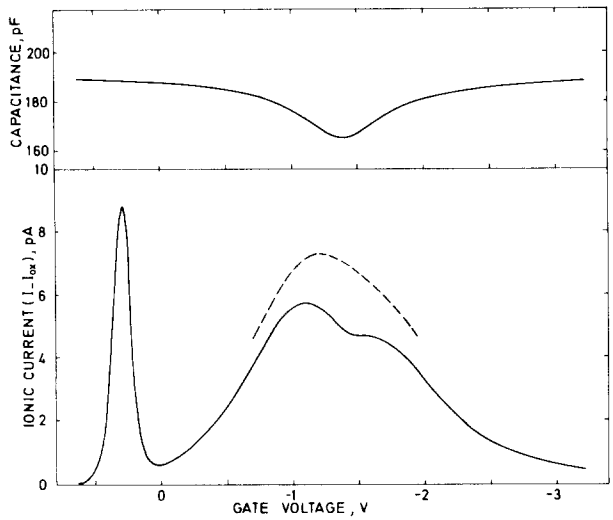

FIG. 2. Example of a TVS measurement (—) in which the K^+ peak is split due to the silicon depletion charge. Measurement of the low-frequency capacitance enables us to reconstruct the undisturbed K^+ peak (---).

The TVS method employs a linear voltage ramp generator which provides the gate voltage V_G to an MOS capacitor at an elevated temperature. The measured current consists of two components: the displacement current of the capacitor and the ionic current. We will consider only the movement of ions from the silicon to the aluminum interface because the detrapping at the silicon interface occurs more readily.[1,5] A typical TVS curve is shown in Fig. 1.

We will now consider TVS measurements of K^+ ions at temperatures at which we expect the majority of the mobile ions to be virtually free to move (as measured with the TSIC technique). The K^+ ions start to move when the field in the oxide is reversed (at $V_G = \phi_{ms}$, the work function difference) and drift to the other interface under influence of the linearly increasing negative gate voltage. We assume that the ions drift with a velocity

$$v(t) = \mu F(t) = \mu \left| \frac{V_G(t) - \phi_{ms}}{d_{ox}} \right|, \tag{1}$$

where μ is the mobility, F is the field in the oxide, V_G is the gate voltage, and d_{ox} is the oxide thickness.

When the ions reach the other interface, the TVS current has a maximum (at $V_G = V_M$).
We now define

$$\Delta V = |V_M - \phi_{ms}| \tag{2}$$

and then the transit time becomes

$$t_{tr} = \Delta V / \alpha, \tag{3}$$

where α is the sweep rate of the voltage ramp. Now

$$d_{ox} = \int_0^{t_{tr}} v(t)\, dt = \frac{\mu\alpha}{d_{ox}} \int_0^{t_{tr}} t\, dt = \frac{\mu\alpha}{2d_{ox}} t_{tr}^2, \tag{4}$$

which provides a value for the mobility:

$$\mu = \frac{2d_{ox}^2 \alpha}{(\Delta V)^2}. \tag{5}$$

III. EXPERIMENT

We have investigated MOS capacitors made by oxidizing 20-Ω cm n-type silicon in a dry O_2 atmosphere during 15 min at 1200 °C($d_{ox} \simeq 1450$ Å) and depositing electrodes by evaporating aluminum from a tungsten-boat. Before the oxidation the furnace was cleaned for 16 h in a 2% trichloroethane/O_2 atmosphere (equivalent to 6% HCl [6] at 1200 °C). This has been shown to reduce both the mobile Na^+ and K^+ concentrations with a factor of about 10^7 and we must conclude that the mobile ions are introduced during the evaporation process. TVS curves were measured in the temperature range 300–450 °C at sweep rates varying from 2 to 1000 mV/s.

At these temperatures the Na^+ ions are in a quasistatic situation: as soon as the field in the oxide changes sign the

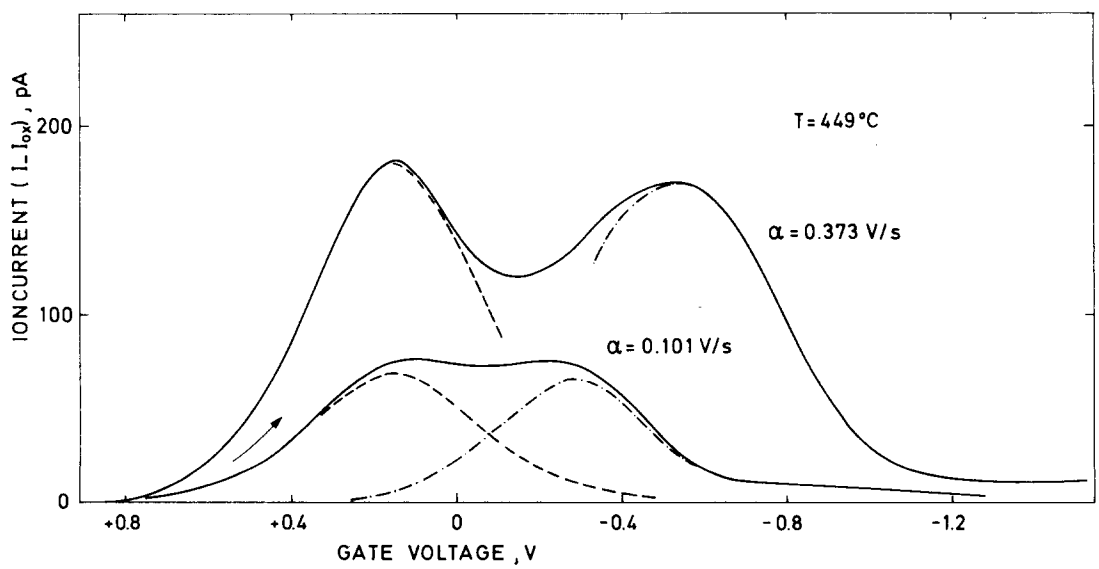

FIG. 3. Example of a TVS measurement (—) in which the Na^+ and K^+ peak overlap. Knowing the quasistatic Na^+ peak (--) enables the undisturbed K^+ peak (---) to be reconstructed.

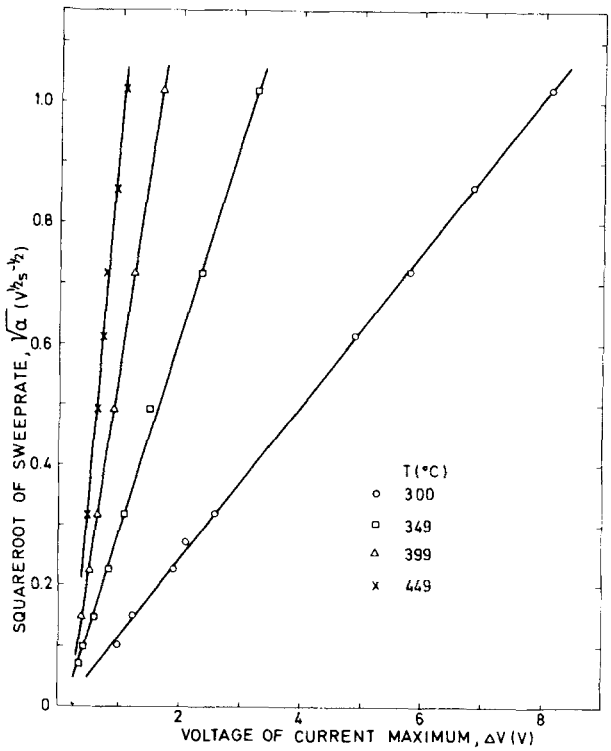

FIG. 4. Relation between the voltage at which the maximum of the K^+ peak occurs and the square root of the sweep rate at different temperatures.

ions drift to the other side of the oxide in a very short time (10 μs at 300 °C). We therefore measure the position of the maximum of the K^+ peak with respect to the maximum of the Na^+ peak. Although in general a TVS curve as depicted in Fig. 1 is found, there may be two complications.

(1) At temperatures below 350 °C, the charge in the silicon depletion layer is not small as compared to the ionic charge. This effects the position of the maximum of the K^+ current only at not too fast and not too slow sweep rates because then the ionic current peak and the C-V dip occur at about the same voltage. Eventually, this causes the K^+ peak to split up in two peaks. In those cases the true K^+ peak was reconstructed by recording a low-frequency C-V curve at that particular sweep rate and adding the silicon depletion current to the measured ionic current (Fig. 2).

(2) At high temperatures and low sweep rates the Na^+ and K^+ peaks overlap. This is because the K^+ ions tend to reach also a quasistatic situation in which a symmetrical peak would result around the voltage at which the field in the oxide changes sign. Knowing the quasistatic Na^+ peak from a measurement at a higher sweep rate and adjusting the Na^+ current with respect to the sweep rates, the K^+ peak is easily reconstructed (Fig. 3).

Now Eq. (5) was verified by plotting V_m versus $(\alpha)^{1/2}$ at different temperatures (Fig. 4). Indeed, straight lines are found and from their slope the mobility μ is calculated. The mobility as a function of the temperature is commonly expressed as

$$\mu(T) = \mu_0 \exp(-E_d/kT), \tag{6}$$

where E_d is the activation energy of drift. In Fig. 5, $\ln \mu$ is plotted versus $1000/T$. A linear regression fit gives the following values

$\mu_0 = 1.16 \times 10^{-2}$ cm^2 V^{-1} s^{-1} (within a factor of 2.5),

$E_d = 1.04$ eV ($\pm$ 0.03).

In Fig. 5, we have also plotted Stagg's[1] results. The extrapolated mobilities are in very good correspondence.

IV. DISCUSSION

Our method is not suited to measure the mobility of Na^+ in SiO_2. This can be explained by noting the emission-limited character of the transport of Na^+ ions.[4] Only the very fast measuring techniques used by Stagg[1] and Kriegler[5] give rise to a current of free Na^+ ions, which is, however, very small.

Our results indicate that K^+ current is transport limited in the temperature range of our experiment. This is bound to lead to one of the following two possibilities.

First, the emission is very fast compared to the transit time. The effect will be that the ions are virtually free to drift when the electrical field changes sign. Such a fast emission, however, is not in correspondence with the results of TSIC measurements, as it would lead to an unlikely high attempt to escape frequency ($> 10^{14}$ s^{-1}).[2,4]

The second possibility is a slower emission (roughly of the same order of magnitude as the transit time), but a large density of conducting states compared to the density of trapping states. In the temperature range used this leads to a

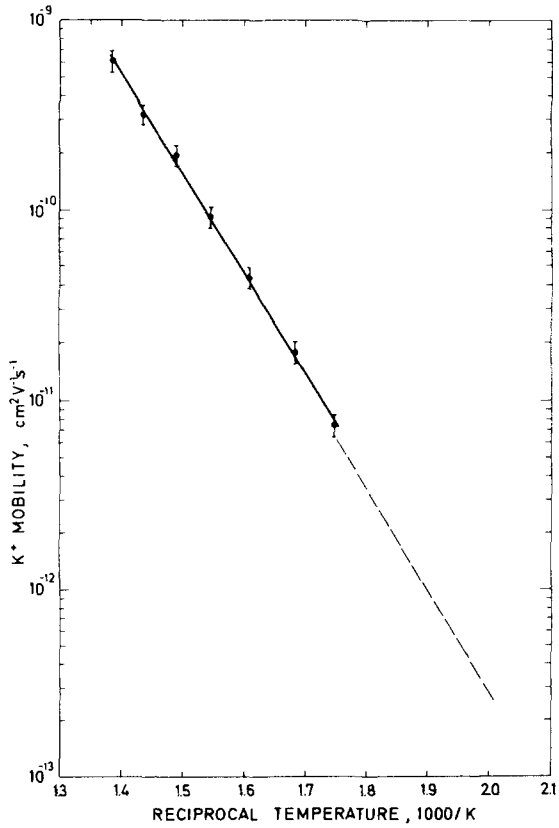

FIG. 5. The mobility of K^+ ions in SiO_2 as a function of the temperature (—): this work; (--): values reported by Stagg.[1]

considerable fraction of the total number of ions in the conducting states. We expect this situation to occur.

The influence of the emission process on the ionic current is to broaden the peak. This leads to an error in the determinatin of V_M of about 5%, which results in a relative error of about 13% in μ. Together with the 10% uncertainty in d_{ox}, which only affects the value of μ_0, the mentioned errors in E_d and μ_0 are determined.

It was shown in Sec. III that the experimental results for μ were fairly well described by an Arrhenius equation. Such an equation was also used previously.[1,5] A more rigorous treatment of the ion transport under the influence of a small electrical field in crystals, however, results in an expression of the form[8]:

$$\mu(t) = (\mu_0^*/T) \exp(-E_d^*/kT). \quad (7)$$

In this model the ions hop from one bulk well into another; E_d^* is the depth of the well and μ_0^* comprises the attempt to escape frequency, the distance of the wells, and an entropy factor.

In the temperature region of our experiment, however, there is a negligible influence of the preexponential term on the exponential character of Eq. (7). Of course, the constants are different:

$$\mu(T) = (17.46/T) \exp(-1.09/kT) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}.$$

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